INFLUENCE OF SUBSTRATE TEMPERATURE ON THE PROPERTIES OF AMORPHOUS CARBON THIN FILMS

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Abstract

Properties of amorphous carbon (a-C) thin films deposited on p-type silicon (*p*-Si), quartz and ITO substrates by microwave (MW) surface-wave plasma (SWP) chemical vapor deposition (CVD) at different substrate temperature (RT~ 300 °C) were analyzed in this work. Argon (Ar: 200 sccm) was used as carrier gas while acetylene (C_2H_2: 20 sccm) and nitrogen (N: 5 sccm) were used as plasma source. Analytical methods such as X-ray photoelectron spectroscopy (XPS), FT-IR and UV-visible spectroscopy were employed to investigate the structural and optical properties of the a-C thin films respectively. FT-IR spectra shows the structural modification of the a-C thin films with substrate temperature showing the distinct peak around 3350 cm^{-1} wave number; which may corresponds to the sp^2 C-H bond. The influence of substrate temperature on film thickness and Tauc optical gap are also noticeable. Tauc optical gap and film thickness both decreased with increasing substrate temperature. The peaks of XPS core level C 1s spectra of the a-C films shifted towards lower binding energy with substrate temperature. We also got the small photovoltaic action of the a-C films deposited at 300 ^{0}C on ITO substrate. a-C thin films were deposited uniformly on all substrates upto 200 ^{0}C and above this temperature Qz and ITO were well deposited but in the case of Si substrates; the films seems to be very thin at 250^{0}C and almost no deposition at 300 ^{0}C. Post deposited a-C thin films were annealed at Nitrogen gas environment with a constant flow of 50 sccm; inside the MW SWP CVD chamber upto 600^{0}C and their properties were studied.

Introduction

Amorphous carbon (a-C) thin films is an interesting material and has been widely investigated in the past decade. It is known that deposition parameters affect the formation of crystalline phase and amorphous structure of a-C thin films. Since the microstructure of a-C thin films is strongly dependent on the deposition conditions, in this study, we discuss the optical, structural and I-V characteristic of a-C thin films deposited by microwave (MW) surface wave plasma (SWP) CVD at different substrate temperatures. On the other hand, the as deposited a-C thin films at room temperature were annealed in nitrogen (N) atmosphere and their properties were studied. The objective of this study is to analyze the influence of substrate temperature and annealing temperature on the properties of a-C thin films in order to optimize the properties of a-C thin films for its possible application on photovoltaic energy conversion.

Film Deposition and Characterizations

We used the MW SWP CVD system for the deposition of a-C thin films. Schematic diagram of the experimental set up of the MW SWP CVD system is shown in Fig. 1. The MW SWP CVD was produced in a 30 cm, cylindrical vacuum chamber by introducing a 2.45 GHz microwave through a quartz window via slot antenna. The microwave introduced through the slot antenna drops exponentially below the quartz window where the electron density exceeds the cut off density [1, 2]. High-density plasma with a uniform electron density of about 10^{11} cm^{-3} formed in the vacuum chamber; broadened in the downward stream region due to the particle diffusion. In brief, MW SWP CVD is a promising plasma source for large area thin film deposition and useful to avoid plasma induced damages of the substrates surfaces [2- 4].

a-C thin-films were deposited at various substrate temperatures ranging from room temperature to 300 ^{0}C on p-type silicon (*p*-Si), quartz (Qz) and ITO substrates. The CVD chamber was evacuated to a base pressure at approximately 9.0×10^{-4} Pa using turbo molecular pumps. Before deposition, the substrates were cleaned beforehand by acetone and methanol for each at 5 minutes in an ultrasonic bath and only Si substrates were etched with diluted hydrofluoric acid (10 %) in order to remove the resistive native oxide layer over the substrates surface. After cleaning, the substrates were dried by N gas and placed quickly on the stage inside the chamber. For film deposition, we used Ar as carrier gas and acetylene (C_2H_2) and N as

plasma sources. The flow rate of Ar, C_2H_2 and N were maintained fixed as 200 sccm, 20 sccm and 5 sccm respectively for the series of experiments. The launched microwave power were typically maintained at 550W throughout the deposition (30 min.) of a-C thin films for all experiments.

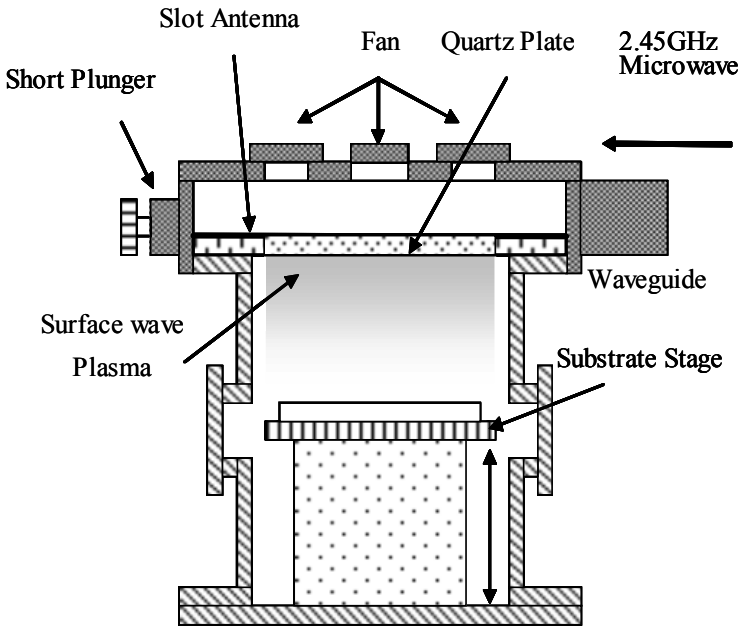


Fig. 1 Schematic diagram of MW SWP CVD system.

The as deposited a-C thin films were annealed for 30 min. inside the MW SWP CVD chamber ranging from 200 ^{0}C to 600 ^{0}C in the nitrogen gas environment by passing the constant flow (50 sccm) of N gas.

JASCO V-570 UV/VIS/NIR spectrophotometer was used to investigate the optical properties of the films. While Nanopics 2100/NPX200 was used to measure the film thickness. The X-ray photoelectron spectroscopy (XPS) was measured by ESCA-3300 KM Electron Spectrometer utilizing an AlKα (hv = 1486.6 eV) radiation as an X-ray source, under high vacuum conditions of about 10^{-7} Pa. While FT-IR spectroscopy measurements were performed in order to study the structural properties of the a-C thin films. Solar simulator (JASCO SS-200W) was employed to characterize photovoltaic properties using Xenon lamp is used as the light source under AM 1.5 illumination condition (100 mW/cm^2) at room temperature.

Results and Discussion

To study the optical characteristics of a-C thin films, reflectance and transmittance of Qz substrates were measured by UV/VIS/NIR spectroscopy in the range of 100-2000 nm. Fig. 2 (a) shows the UV/VIS/NIR transmission spectra of a-C thin films deposited at various substrate temperatures. The transmission spectrum of a-C thin films deposited at 300 ^{0}C shows the lowest % transmission in the visible wavelength region. While the % transmission obtained from the a-C films deposited at 200 and 250 ^{0}C almost overlap in the visible region and the film deposited at room temperature shows the highest % transmission. This result may lead to conclude that the a-C thin film prepared at 300 0C substrate temperature has the maximum photon absorbance in the visible region. Figure 2 (b) is the plot of % transmission vs. wavelength of a-C thin films on quartz of as deposited at room temperature and annealed at various temperatures ranging from 200 ^{0}C to 600 ^{0}C. The percentage transmission decreases sharply from as deposited to annealed at 600 ^{0}C. This behavior is clearly reflected in the optical band gap.

In order to calculate the optical band gap of the a-C thin films, optical transmission and reflectance were measured by UV/VIS/NIR spectroscopy in the range of 100-2000 nm using Qz substrates. The absorption coefficient (α) was calculated by the spectral reflectance and transmittance, and the film thickness data.

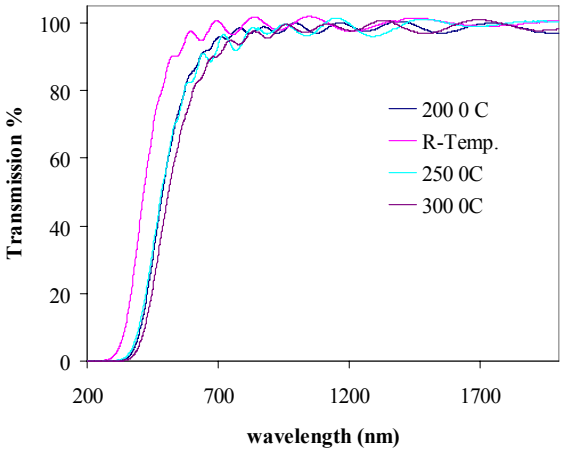


Fig. 2 (a)

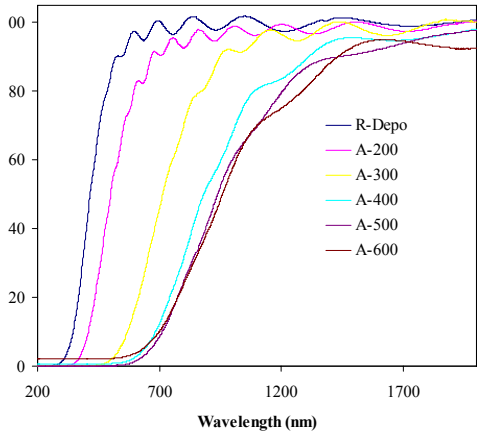


Fig. 2 (b)

Fig 2 UV/VIS/NIR transmission spectra of a-C thin films: **(a)** deposited at various substrate temperatures; **(b)** deposited at room temperature and annealed in N environment.

Optical band gap was obtained from the extrapolation of the linear part of the curve at $\alpha = 0$ by using the Tauc equation: $(\alpha h\nu)^{1/2} = B(E_g - h\nu)$; conventionally defined for amorphous semiconducting materials. The optical gaps were tuned from 2.4 to 1.9 eV from room temperature to 300 ^{0}C deposition. The detail figures of the optical gaps with different substrate temperatures are given in table 1(a). Films' thickness and optical gap both decreases with substrate temperatures. This temperature dependence is may be due to the etching of the films by atomic hydrogen. Growth itself is independent to substrate temperatures [5]. Table 1 (a) shows the decrease of films' thickness which may be interpreted as the increased rate of etching due to the increase of temperature. Above 300 ^{0}C no deposition was successed at the above mentioned deposition conditions. The detail figures of films' thickness and optical gaps of annealed a-C thin films are summarized in table 1 (b). The films deposited at room temperature were annealed from 200 ^{0}C to 600 ^{0}C.

Table1: (a) Optical gap and film thickness of a-C thin films at different deposition temperatures;
(b) Optical gap and film thickness of annealed a-C thin films.

Table 1(a)

Deposition Temperature (^{0}C)	Thickness (nm)	Optical Gap (eV)
Room Temperature	1434	2.4
200	1229	2.1
250	902	2.1
300	570	1.9

Table 1(b)

Annealing Temperature (^{0}C)	Thickness (nm)	Optical Gap (eV)
200	1319	2.0
300	1226	1.4
400	921	1
500	834	0.9
600	722	0.9

Thickness of the films decreases from 1434 nm (as deposited) to 722 nm (annealed at 600 ^{0}C) and optical band gaps are also decreased from 2.4 eV to 0.9 eV.
It is reported that thermal annealing causes the evolution of hydrogen (H) from the film. Table 1 (b) shows that the thickness of a-C films annealed 400 ^{0}C decreases from 1434 nm to 921 nm indicating main

evolution starts from this temperature. The decrease of the thickness of a-C films may be due to the evolution of either molecular H or hydrocarbon molecules. In this condition, the rearrangement of C-C network occurs [5] and hence this rearrangement causes the optical gap to start to close up.

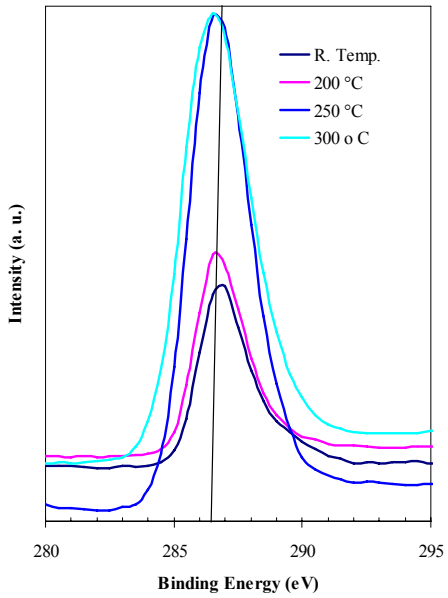


Fig 3 (a)

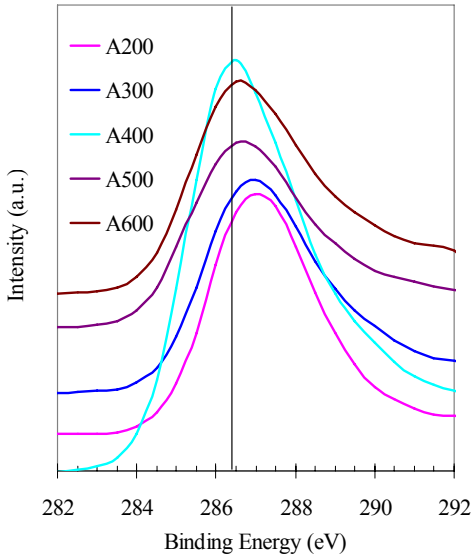


Fig. 3 (b)

Fig. 3 Core level XPS spectra of C 1S of a-C: **(a)** deposited at various substrate temperatures. **(b)** annealed at various temperature.

XPS was used to investigate the chemical bonding and structural properties of a-C thin films. Although there are still some controversies about the assignments of the individual components of the C 1s and N 1s core level spectra [6-9], the XPS analysis is one of the most likely used technique in the literatures to characterize the chemical bonding structures and to acquire useful information on the chemical environment of a-C thin films [8, 9]. Fig. 3 (a) shows the core level XPS spectra of a-C thin films deposited at various substrate temperatures. The core level C 1s spectra of a-C thin films deposited at room temperature is centered at 286.5 eV binding energy while others shifted towards lower binding energies. The peak of the spectra obtained from the films deposited at 250 ^{0}C and 300 ^{0}C almost centered to the same binding energy indicating the same character. These results from XPS measurements clearly indicate the change of bonding structure of the a-C thin films and can be concluded the best near graphitic order is the a-C thin film obtained at 250 ^{0}C and 300 ^{0}C for its possibilities to use as photovoltaic application. Fig. 3 (b) shows the XPS C 1S spectra of the a-C thin films annealed at different temperatures ranging from 200 ^{0}C to 600 ^{0}C. The peak of C 1S of the a-C thin films annealed at 200 ^{0}C and 300 ^{0}C almost centered at same binding energy while others shifted towards lower binding energies. The spectra of a-C thin films annealed at 500 ^{0}C and 600 ^{0}C shows the almost same characteristics; which can be correlated with optical properties. Fig. 4 shows the atomic concentration of N with respect to annealing temperature of the a-C films. As deposited a-C thin films contain 18.20 % N (atomic.) and it is almost independent to the annealing temperatures. The film annealed at 500 ^{0}C shows the high percentage (22.16) of N content. The reason that why such slight changes occur in N concentration in the films is yet to be discussed.

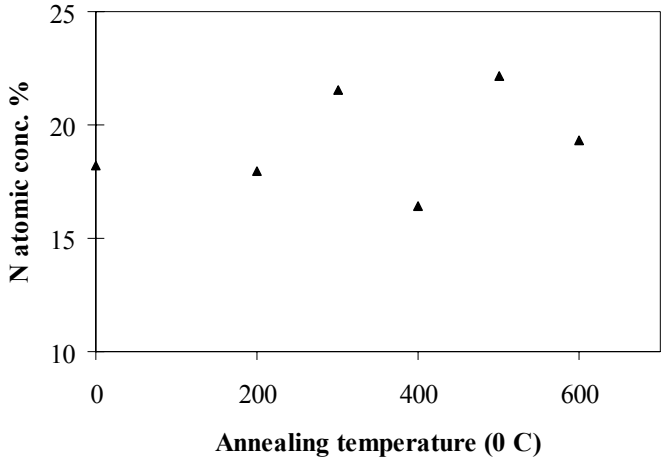
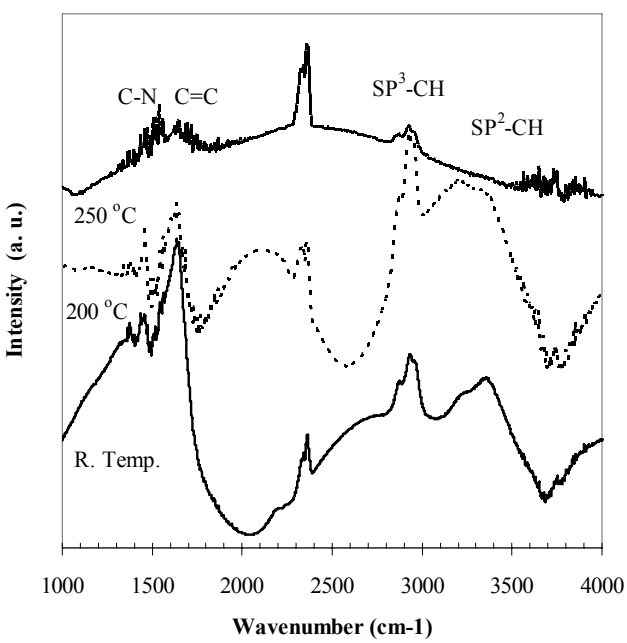


Fig. 4 Annealing temperature vs. N atomic conc. %

According to the classification of amorphous carbon nitride thin films by A. C. Ferrari et al. [10]; we believe that our a-C thin films to be in the category of plasma deposited a-C:H:N with moderate sp^3 content. In a-C thin films, FT-IR is used to study the bonding preference of hydrogen to C or N sites [11]. Fig. 5 (a) the IR spectra of a-C thin films deposited at different substrate temperatures.1000 – 2000 cm^{-1} wavenumber may be referred as the features due to skeletal C ═ C and or mixed C ═ N modes. The spectra show the qualitative changes of these modes with respective deposition temperatures from room temperature to 200 ^{0}C. But the spectrum which corresponding to 250 ^{0}C is little bit different which may be due to the thin film thickness on Si. At and above 250 0^C substrate temperatures the a-C films on Si seems very thin but well deposition were occurred on Qz and ITO up to 300 ^{0}C.



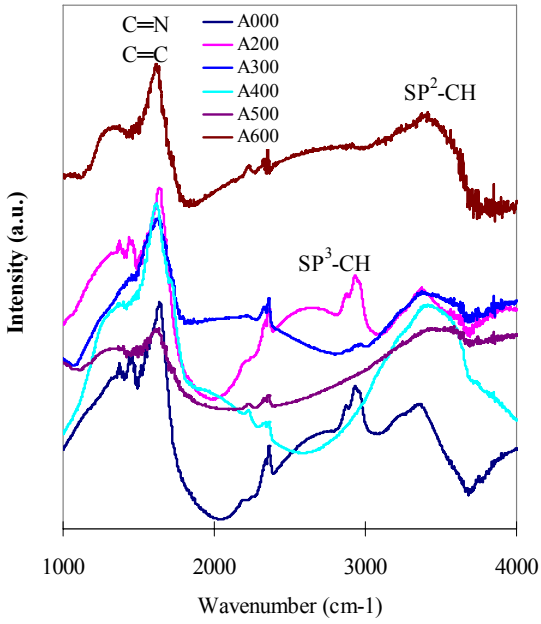


Fig. 5 (b)

Fig 5 (a)

Fig (5) FTIR spectra of a-C thin films: **(a)** deposited at various substrate temperatures **(b)** annealed at various temperatures.

In addition, the peaks around 3350 cm $^{-1}$ are due to the SP^2C-H related bands which is more prominent in the case of the film deposited at 200 ^{0}C. Fig. % (b) shows the FTIR spectra of the annealed samples ranging from 0 to 600 ^{0}C. The films annealed at 400 ^{0} C shows the most prominent peak which refers to SP^2-CH. A gradual decrease of the intensity of the peak around 2950 cm^{-1} wavenumber, which refers to SP^3 C-H, occurs with increase in annealing temperatures. This result is correlated with other characterizations mentioned above.

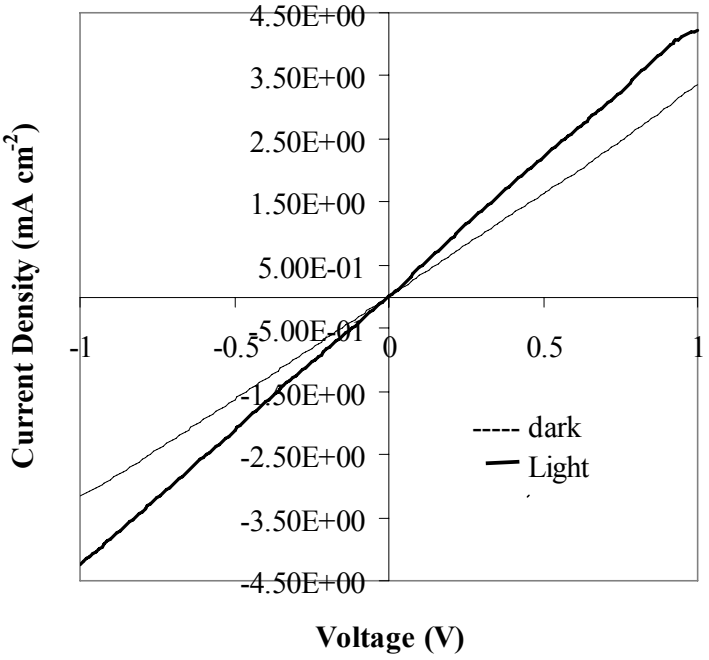


Fig. 6 I-V characteristics of Au-a-C/ITO structure of the a-C thin film deposited at 300 ^{0}C

A small photoconductivity action is obtained from the Au-a-C/ITO structure of a-C deposited at 300 ^{0}C substrate temperature under light illumination. Some folds of current density is increased under light illumination. However, the photoconductivity is still low to fabricate the a-C based solar cell; this work would be the important reference for the future work.

Conclusion

The a-C thin films were deposited on p-Si, ITO and Qz substrates by MW SWP CVD technique at various substrate temperatures. On the other hand, as deposited a-C thin films were annealed up to 600 ^{0}C in N atmosphere. The optical structural and electrical properties of the a-C thin films were characterized using standard scientific techniques. Lowest optical gap (1.9eV) was obtained from the a-C thin films deposited at 300 ^{0} C temperature while annealed samples showed the sharp decrease of the optical gap. The deposition rate was found to be decreased with substrate temperature. While annealing, thickness of the films decreases due to the evolution of H from the films. XPS and FTIR characterization were performed in order to study the structural properties of the films. Photovoltaic action is obtained from the Au-a-C/ITO structure of a-C deposited at 300 ^{0}C substrate temperature. However, the photoconductivity is still low to fabricate the a-C based solar cell; this work would be the important reference for the future researches.

References

1. 1. M. Nagatsu, G. Xu, I. Ghanashev, M. Khanoh, H. Sugai, 1997, Plasma Sources Sci. Technol. 6, 427.
2. M. Nagatsu, T. Sano, N. Takada, N. Toyoda, M. Tanga, H. Sugai, 2002, Diamond Relat. Mater. 11, 976.
3. A.M.M. Omer, S. Adhikari, S. Adhikary, H. Uchida, M. Umeno, 2004 Diamond Relat. Mater. 13, 2136.
4. S. Adhikari, S. Adhikary, A.M.M. Omer, M. Rusop, H. Uchida, T. Soga, M. Umeno, 2005,Diamond Relat. Mater. 14, 1824.
5. J. Robertson, 2002, Material Science and Engineering R 37, 129-281
6. D. H. A. Blank, R. P. J. Ijsselsteijn, P. G. Out, H. J. H. Kuiper, J. Floksura, H. Rogalla, 1992, Mater. Sci. Eng. B 13, 67.
7. Y. Nishikawa, K. Tanaka, Y. Yoshida, 1991, Nippon Kinzoku Kaishi, 55, 581.
8. F. L. Freire, D. F. Franceschine, 1997, Thin Solid Films 293,236.
9. M. Rusop, A. M. M. Omer, S. Adhikary, T. Soga, T. Jimbo, M. Umeno, 2005, J. Non-Cryst. Solids 351, 2562.
10. A. C. Ferrari, S. E. Rodil, J. Robertson, 2003, Phys. Rev. B 67, 155306-1-155306-20.